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Conductive and Tribological Properties of Lithium-Based Ionic Liquids as Grease Base Oil

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This article reports several conductive greases prepared by ionic liquids (ILs) that are synthesized by mixing lithium tetrafluoroborate (LiBF$_4$) or lithium bis(trifluoromethanesulfonyl) imide (LiNTf$_2$) in diglyme (G2) and tetraglyme (G4) with appropriate weight ratios at room temperature (RT). The ILs have good solution in poly(ethylene glycol-ran-propylene glycol) monobutyl ether (PAG) and thus can be used as a base oil for preparing grease for steel–steel contacts. The electrical conductive properties of the grease prepared with the mixed oil of PAG plus ILs were evaluated using the DDSJ-308A conductivity tester, GEST-121 volume surface resistance tester, and HLY-200A circuit resistance tester. Combining the free volume with viscosity, the conductivity is inversely proportional to viscosity. The tribological properties were investigated using an MFT-R4000 reciprocating friction and wear tester. The results demonstrated that the prepared greases possess better conductive and tribological properties than the commercial grease with Cu powder as an additive.

KEY WORDS

Grease; Ionic Liquid; Tribology; Conductivity; Contact Resistance; Volume Resistivity

INTRODUCTION

Lubricating grease, with excellent antiwear and friction reduction properties, is the most widely used lubricant for machine equipment to protect components from friction and wear (Wang, et al. *(1)*, *(2)*). However, few articles relating to conductive lubricating greases were found in the published literature. When the lubricating greases are applied in the conductive parts of electrical equipment, such as electrical switches, integrated circuits, microelectronic mechanical systems, power machines, and power transmission and transformation equipment (Tu, et al. *(3)*), the conductivity of the lubricating greases becomes particularly important. Compared to expansive conductive metal powders, such as gold, silver, copper, alloy, and tin, ionic liquids (ILs) have unusual characteristics, such as wide liquid-phase range, nonflammability, negligible volatility, high conductivity, and high thermal and chemical stability (Qu, et al. *(4)*; McCrary and Rogers *(5)*; Street, et al. *(6)*), and have received significant attention as lubricants in recent years (Morales, et al. *(7)*; Zhao, et al. *(8)*; Song, et al. *(9)*). Fan, et al. *(10)* found that new ILs could be obtained simply by adding lithium salts (LiX) to polyethylene glycol and the new ILs showed even more effective tribological properties than those of conventional ILs. The ILs can enlarge the conductive grease application (Fan, et al. *(11)*).

In this article, the base oil was the mixture of PAG and ILs. The conductive and tribological properties were investigated in detail and compared with the commercial grease with Cu powder as an additive.

EXPERIMENTAL DETAILS

Materials and Preparation

The PAG used in this study was purchased from Dow Chemical (China) Investment Company. The diglyme (G2) and tetraglyme (G4) were obtained from the State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics. The PTFE micropowder had a grain size of about 4 μm (Dyneon TF9207) and density of 2.2g/cm^3. The lithium salts (LiBF$_4$ 99 wt% and LiNTf$_2$ 99 wt%) were obtained from Shanghai Energy Lithium Industrial Company. The acetone was obtained from Sinopharm Chemical Reagent Co., Ltd. All chemical reagents used in this study were of analytical grade and without further purification. Figure 1 shows the reaction between lithium salts and G2 and G4 to forming ILs, respectively.

The ILs used as base oil were synthesized by adding an appropriate weight of the lithium salts into the G2 and G4 and stirring vigorously until the lithium salts dissolved completely to form the ILs. Li$^+$ can form complexes with G2 and G4, generating weak Lewis acid complex cations [Li(G2)]$^+$ and [Li(G4)]$^+$, which can form novel ILs (Li(G2)X and Li(G4)X) with the weak Lewis basic anions (BF$_4^-$ and NTf$_2^-$) of lithium salts (Song, et al. *(12)*). The weight ratio of lithium salts/G2 or G4 is 1/1. The typical properties of the lithium salts and conductive properties of PAG and ILs are shown in Tables 1 and 2, respectively.

The base oils for preparing greases were PAG, PAG+Li(G2)BF$_4$ IL, PAG+Li(G2)NTf$_2$ IL, and PAG+Li(G4)NTf$_2$ IL, respectively, and the lubricating greases were synthesized according to the following procedures. First, the base oil was added into

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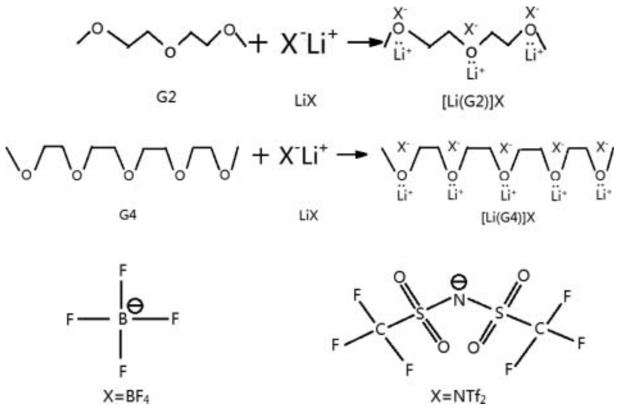


Fig. 1—Reaction between lithium salts and G2 and G4.

the corresponding vessel and stirred at room temperature. Second, the PTFE was slowly added into the base oil under vigorous stirring. When the base oil and the PTFE were mixed uniformly, a certain amount of the acetone was injected and stirred for about 30min to ensure that the PTFE was completely dispersed in the base oil. Then the mixture was heated up to 80°C and maintained at this temperature for about 30min to remove the acetone. Finally, the mixture was cooled to room temperature, and then the PAG grease, [Li(G2)]BF_4 grease, [Li(G2)]NTf_2 grease, and [Li(G4)]NTf_2 grease were obtained after three separate fine grinding/homogenization steps in a three-roller mill.

Characterizations and Tribological Test

The dropping point of the lubricating greases was characterized according to the national standard GB/T 3498. The penetration was characterized according to the national standard GB/T 269. The copper strip tests of the lubricating greases were performed by the national standard GB/T 7326. The conductivity, volume resistivity, and initial and final contact resistance were valued using a DDSJ-308A conductivity tester, GEST-121 volume surface resistance tester, and HLY-200A circuit resistance tester made by Beijing Guance Testing Instrument Co., Ltd., respectively.

The MFT-R4000 reciprocating friction and wear tester was employed to investigate the tribological performance of the prepared grease at various loads with a ball-on-disc configuration at room temperature for 30min. Contact between the frictional pairs was achieved by pressing the upper ball (diameter 5mm, AISI 52100 steel, hardness 710 HV) against the lower stationary steel discs (ø 24 × 7.9mm, AISI 52100 steel, with a hardness of about 400 HV). The loads were 50, 100, and 150N; the frequency was 5Hz and the stroke was 5mm. All of the disc specimens and steel balls were cleaned in petroleum ether using an ultrasonic cleaner for 2 min, before and after each tribotest. The friction coefficient was recorded automatically by a computer connected to the MFT-R4000 tester. Three repetitive measurements were performed, and the average values with error bars are reported in this article.

TABLE 1—TYPICAL PROPERTIES OF THE LITHIUM SALTS

Sample	Melt Point (°C)	Density (kg/m^3)	Formula Weight
$LiBF_4$	296.5	852	93.74
$LiNTf_2$	236	1334	287.08

TABLE 2—CONDUCTIVITIES OF PAG AND ILS

Sample	PAG	[Li(G2)] BF_4 IL	[Li(G2)] NTf_2 IL	[Li(G4)] NTf_2 IL
Conductivity (μs/cm)	0	1,014	712	706

RESULTS AND DISCUSSION

Physical–Chemical Characteristics and Conductive Properties of the Greases

Table 3 lists the typical properties of the prepared greases. The PAG grease's dropping point is 281°C and has a good corrosion resistance property (copper corrosion 1a). The PAG+ILs grease can improve the dropping point of the greases and has a slight effect on the copper corrosion of the greases. Table 4 lists the conductive properties of the greases. The relationship between conductivity and volume resistivity is basically reciprocal. The commercial grease with Cu powder as a conductive additive has conductivity too low to detect. The conductivity increases five and eight orders of magnitude, respectively, compared to PAG grease and the commercial grease. Moreover, the contact resistance reduces to one third that of the PAG grease. When used in the conductive parts of electrical equipment, the higher conductivity leads to a lower voltage drop. In addition, the higher conductivity can lead to the lower heat product while current transmission and reduces the metal equipment oxidation rate. Therefore, the conductive grease can extend the service life of conductive equipment, reduce costs, and conserve energy. The conductive grease also has a relatively low stabilizing coefficient, which can reduce the variation amplitude of resistance and thus make the current more stable.

In a composite polymer electrolyte solution, the conductivity behavior mainly depends on local relaxation and polymer chain segment motion, and transmission mainly occurs in the amorphous phase area. The ion transport diagram is shown in Fig. 2 (Armand, et al. *(13)*). Polymer chain segment motion leads to Li^+ polymer coordination bond fracture, resulting in diffusion of the metal cations and transition in the local electric field effect. Because the Li ion radius is very small, if the negative ion radius

TABLE 3—PHYSICAL PROPERTIES OF THE GREASES

Sample	Dropping Point (°C)	Penetration (1/4 mm)	Copper Corrosion (T2 copper)
Commercial grease	290	57.7	1b
PAG grease	281	89.9	1a
Li(G2)BF_4 grease	334	88.5	1b
Li(G2)NTf_2 grease	331	86.4	1b
Li(G4)NTf_2 grease	336	109.6	1b

TABLE 4—CONDUCTIVE PROPERTIES OF THE GREASES

Sample	Commercial Grease	PAG Grease	Li(G2)BF$_4$ Grease	Li(G2)NTf$_2$ Grease	Li(G4)NTf$_2$ Grease
Conductivity (μs/cm)	0	0	625	319	310
Volume resistivity (Ωcm), 20°C	1.34e11	1.25e8	1.97e3	3.35e3	3.69e3
Initial contact resistance (uΩ)	110.2	93.6	39.3	38.9	50.1
Final contact resistance (uΩ)	110.8	94.0	39.5	39.1	50.2
Stabilizing coefficient	1.005	1.004	1.005	1.005	1.002

is large, the lithium salt dissociation energy is low and ionization is easy.

According to the free volume model, polymer with necessary space for ion mobile, and the ion must overcome the energy of the interaction between polymer chains when migrating, and when it comes to grease, the ion also need to overcome the energy of the thickener attraction E_{attr}. The relationship between conductivity σ and free volume V_f and temperature T is (Du *(14)*):

$$\sigma = \sigma_0 exp\left[-\left(\frac{rV^*}{V_f} + \frac{E_\sigma}{K_B T} + E_{attr}\right)\right] \quad [1]$$

where σ_0 is constant, its value is closely related to the electric field intensity; r is a constant for a single substance and is an overlap factor which should lie between 0.5 and unity; V^* is the necessary minimum required volume of the void; V_f is the specific free volume; K_B is Boltzmann constant; T is the temperature; E_σ is the activation energy for electrical conduction (Vila, et al. *(15)*):

$$E_\sigma = \frac{nW_0 T_g}{2W} \quad [2]$$

where n is a number of the order of the number of neighbor particles; $\frac{W_0}{W}$ is the fraction of the number of states of wave vector near the reciprocal particle distance respecting the total number of states; T_g is the glass transition temperature.

The viscosity ϕ can be related to the free volume (Yu, et al. *(16)*):

$$\phi = CT^{0.5}\exp\left(\frac{rV^*}{V_f}\right) \quad [3]$$

with C as a constant. Then Eq. [1] can be rewritten as

$$\sigma = \frac{\sigma_0 CT^{0.5}}{\phi}\exp\left(-\frac{E_\sigma}{K_B T} + E_{attr}\right) \quad [4]$$

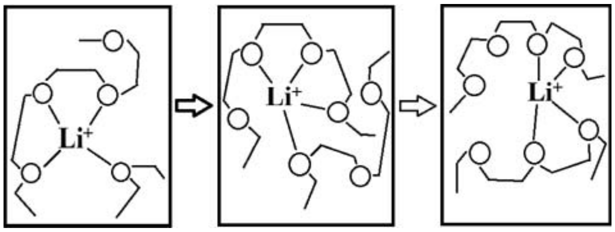


Fig. 2—Ion transport diagram.

We can see that the grease conductivity is inversely proportional to viscosity. Above the glass $T_g$ransition temperature T_g, the polymer chain relaxation take thermal motion, and the free volume changes with temperature, $\frac{rV^*}{V_f}$ is variable; and the conductivity related to the viscosity, the activation energy, and the thickener attraction. Below the glass transition temperature T_g, the polymer chain relaxation is frozen, $\frac{rV^*}{V_f}$ is a constant lead the viscosity not changing, and the relationship between grease conductivity σ and temperature T is Vogel-Tamman-Fulcher (VTF) type equation (Gray and Armand *(17)*; Ye and Elabd *(18)*):

$$\sigma; = \sigma_0 \exp\left(-\frac{\mathrm{E}_\sigma}{\mathrm{K_B T}} + \mathrm{E_{attr}}\right) \quad [5]$$

Free volume model only considering the relationship between ion and ionic conduction volume. In terms of conductive grease, the thickener attraction E_{attr} may lead to more energy needed when ion migrating, which leads to the lower conductivity for the grease than the ILs. However, the equation of the conductivity is still a VTF type, which is simple and can be widely used.

Tribological Test Results

The friction coefficients and wear volume of the lubricating greases under various applied loads are shown in Fig. 3. The friction coefficients of the greases prepared with PAG+ILs all had better friction reduction properties under the three loads than the commercial grease and PAG grease, and the Li(G4)NTf$_2$ grease performed the best. The results of the wear volumes clearly demonstrated that the prepared greases possessed excellent antiwear performance compared to the commercial grease during the 30-min testing time. For the prepared greases, the PAG+ILs grease can improve the antiwear properties of the PAG grease at all three loads, and the lower wear volume values might be a result of the chemical reaction film (Kajdas *(19)*). However, the wear volume reductions of the three PAG+ILs grease are similar, indicating that the antiwear properties of the three ILs are similar.

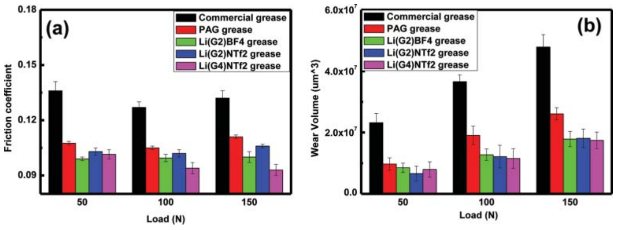


Fig. 3—(a) Friction coefficients and (b) wear volume of the greases under various loads. (Color figure available online.)

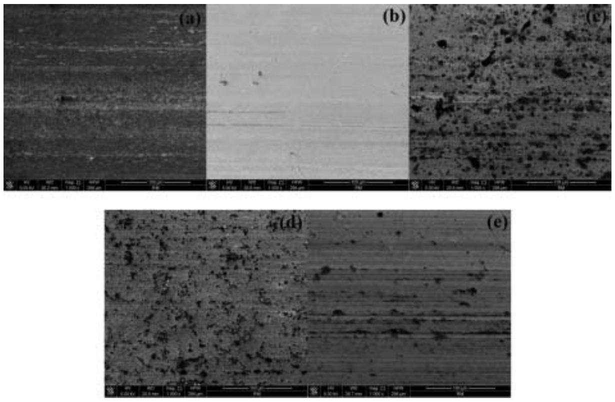
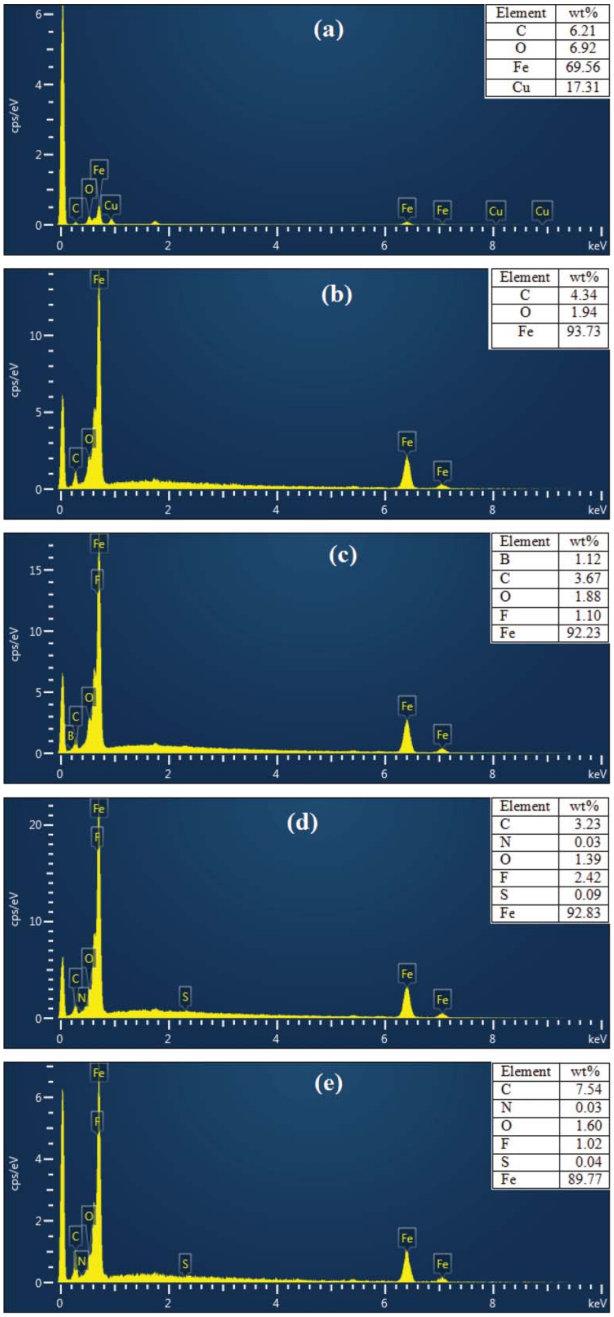


Fig. 4—Scanning electron microscope morphologies of the worn surfaces lubricated by different lubricants under a load of 150N: (a) commercial grease, (b) PAG grease, (c) [Li(G2)]BF4 grease, (d) [Li(G2)]NTf2 grease, and (e) [Li(G4)]NTf2 grease.

The scanning electron microscope morphologies of the worn surfaces under the lubrication of the greases at 150 N are shown in Fig. 4. The worn surface lubricated by the commercial grease (Fig. 4a) was quite rough with many grooves, adhesive wear, and corrosion spots. The worn surfaces lubricated by PAG greases (Fig. 4b) are quite smooth with shallow grooves. However, the worn surfaces lubricated by PAG+ILs greases (Figs. 4c–4e) were quite rough and have many adhesive wear and corrosion spots.

In order to investigate the friction and wear mechanism and the elements in the tribofilm, energy-dispersive X-ray spectroscopy (EDS) analysis was employed to further clarify the chemical component of several typical elements on the worn surface. Figure 5 shows the EDS of the typical elements on the worn surface lubricated by the commercial grease and the prepared grease under a load 150N.

The high concentration of Cu element (Fig. 5a) may be responsible for the high friction coefficient and large wear volume. The peaks in Figs. 5c–5e confirmed the existence of B, F, S, and N, it is concluded that some B, F, S, and N ions were incorporated into the surface film formed by the chemical reactions that occurred on the wear surface in the friction process. The weight ratio of LiNTf2/G2or G4 is 1/1, which is nearly the molar ratio of 0.5/1 and 0.8/1, and because the LiNTf$_2$ and G2or G4 can active with a molar ratio of 1/1 (Song, et al. *(12)*), less ILs can be formed in G2 than in G4 at a certain weight. The weight ratio corresponding to F and S element-related compounds was less in Fig. 5e than in Fig. 5d, and it is concluded that more LiNTf$_2$ were incorporated into the ILs formed by LiNTf$_2$ and G4 than by LiNTf$_2$ and G2, and the greater ILs are responsible for the lower friction coefficient, which significantly contributes to the friction-reducing properties of the lubricating grease.



Element	wt%
C	6.21
O	6.92
Fe	69.56
Cu	17.31

Element	wt%
C	4.34
O	1.94
Fe	93.73

Element	wt%
B	1.12
C	3.67
O	1.88
F	1.10
Fe	92.23

Element	wt%
C	3.23
N	0.03
O	1.39
F	2.42
S	0.09
Fe	92.83

Element	wt%
C	7.54
N	0.03
O	1.60
F	1.02
S	0.04
Fe	89.77

Fig. 5—EDS of the elements on the worn surface lubricated by (a) the commercial grease, (b) PAG grease, (c) [Li(G2)]BF4 grease, (d) [Li(G2)]NTf2 grease, and (e) [Li(G4)]NTf2 grease at 150N.

CONCLUSIONS

Several conductive greases that can be used for electrical contact equipment have been synthesized. The conductive test results show that these greases have excellent conductive properties. The conductivity increases five and eight orders of magnitude compared to PAG grease and the commercial grease with Cu powder as a conductive additive, respectively. Moreover, the contact resistance reduces to one third that of the PAG grease. Combining the free volume with viscosity and thickener attraction, the conductivity of grease is still a VTF type equation and is inversely proportional to viscosity. The tribotest results show that these greases have excellent friction-reducing and antiwear properties for the lubrication of steel–steel contacts. The tribological properties are greatly improved when compared to commercial grease. Moreover, these greases can be synthesized easily and require no more separation or purification, which makes them less expensive. It is expected that these conductive greases could have a potential use for the conductive parts of electrical equipment, such as electrical switches, integrated circuits, microelectronic mechanical systems, power machines, and power transmission and transformation equipment.

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